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Note

Infrared Studies on Molecular Orientation in Nematic Films of MBBA with Two Free Surfaces

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It is known that the molecular orientation in a nematic liquid crystal is strongly dependent on the properties of the solid surfaces to which the liquid crystal directly attaches. Many studies along this line have been carried out by means of a polarizing microscope, infrared spectroscopy and other methods. However, so far only a little work has been done on the molecular orientation in a nematic film with two free surfaces, although orientation properties of liquid crystal itself are very important to have informations about the interaction among liquid crystal molecules.

Faetti and Fronzoni[1] have observed the nematic films of N-(p-methoxybenzylidene)-p-butylaniline (MBBA) with two free surfaces by polarizing microscope and found that there are three different structures depending on the film thickness. The films thicker than 70 μm are characterized by appearance of bright textures and some disclination lines under a polarizing microscope, suggesting that the orientation of the molecular axes is not uniform throughout the sample and the director (the average of a distribution of the molecular axes) is tilted with respect to the normal axis to the film surface. When the thickness is reduced to 70–10 μm, the film becomes uniformly dark under the crossed polarizers. Thus the director is thought to be uniaxially oriented around the normal axis to the surface (homeotropic). If the thickness is further reduced to a value so called critical thickness ($\sim$10 μm), the film gives birefringence colours. In this structure, the director may be nearly parallel to the film surface. In this work, we have studied infrared spectroscopically the changes in molecular orientation due to the film thickness of nematic film of MBBA with two free surfaces.

Experimental apparatus used was similar to that devised by Faetti and Fronzoni,[1] and is shown in Fig. 1. The films with two free surfaces were obtained by horizontally suspending a nematic drop by a rectangular frame made of two nylon wires and two platinum clips. The film thickness could be controled by changing the amount of the drop and the distance between the two platinum clips. Since, after suspending

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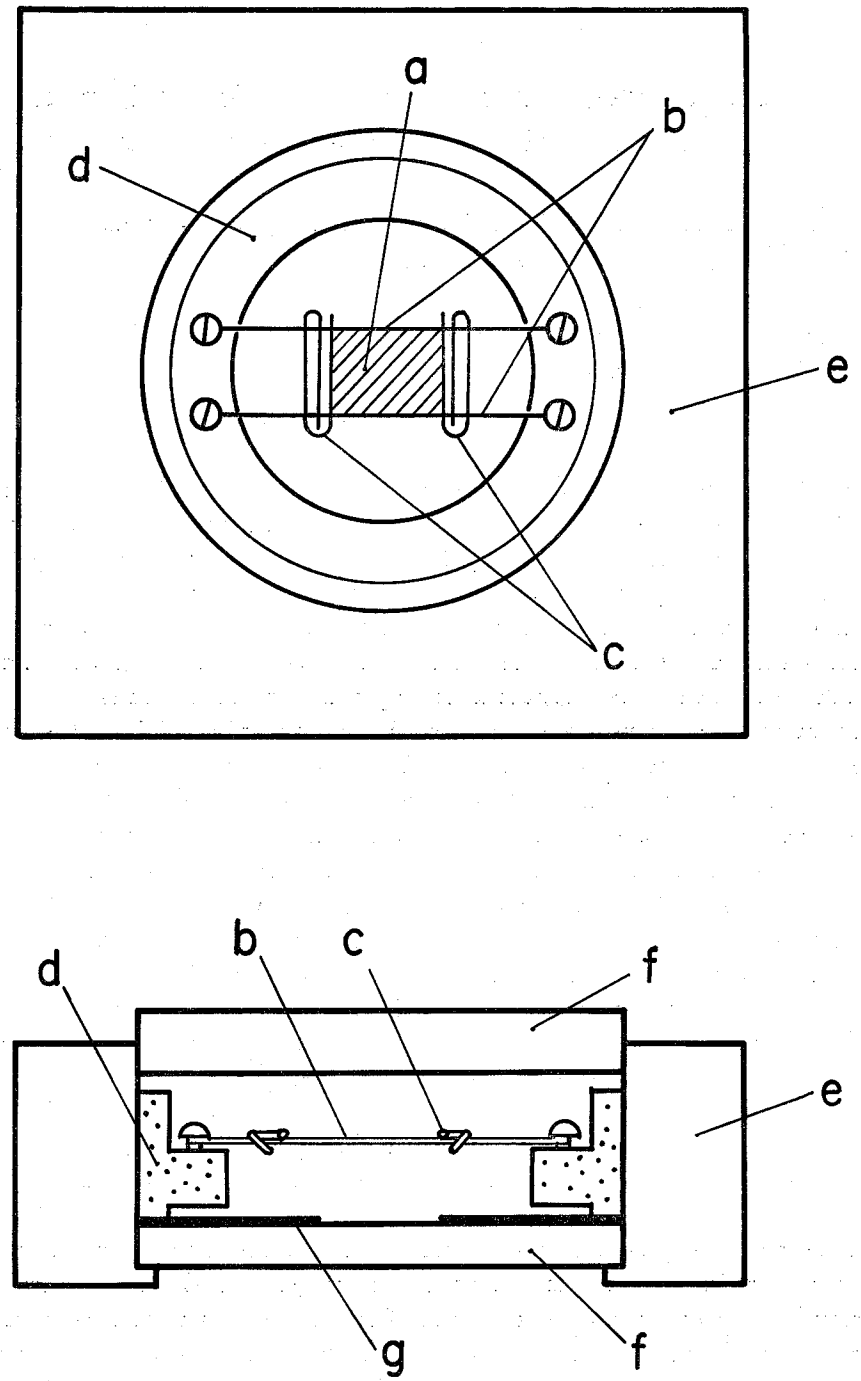

Fig. 1. Experimental apparatus. (a) Sample film, (b) Nylon wires, (c) Platinum clips, (d) Cu-ring, (e) Thermostatic box, (f) KBr plates, (g) slit.

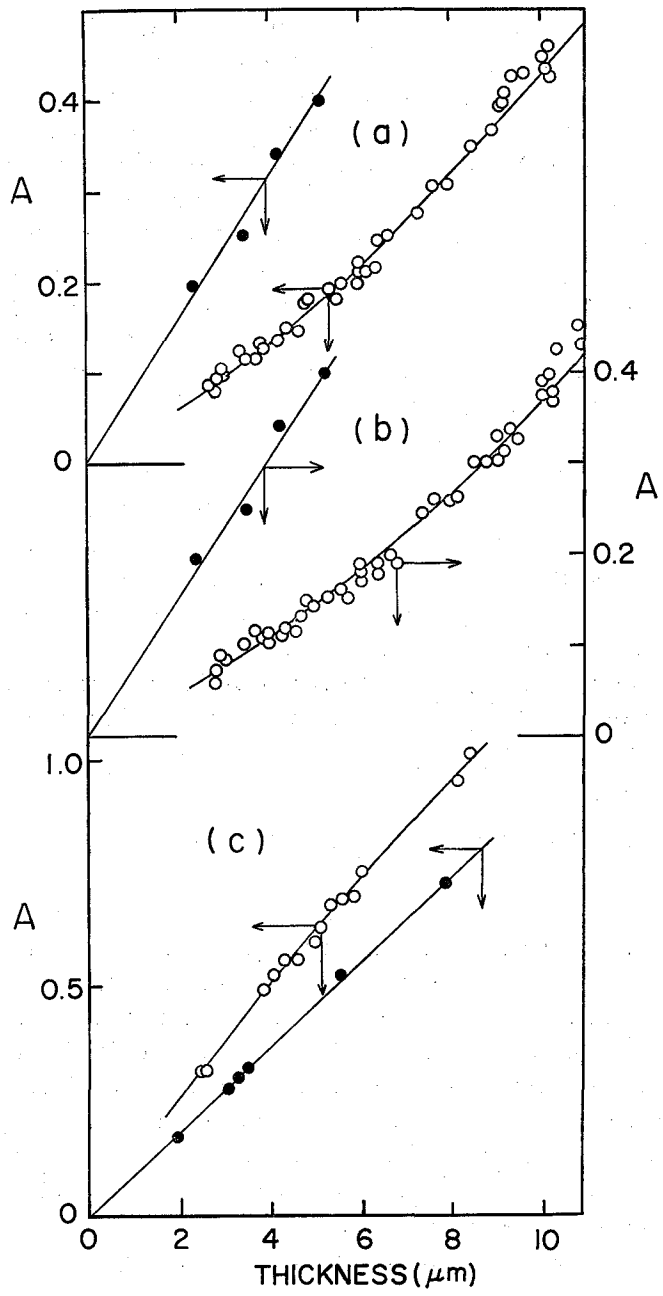

Fig. 2. Absorbance *vs.* thickness plots for the bands at (a) 1626, (b) 1573, and (c) 833 cm^{-1}.
—●— isotropic, —○— nematic.

the sample, the film became gradually thinner and came to an equilibrium thickness, the films were kept at constant lengths for about ten minutes before measurements. Film thickness was estimated from the interference fringes observed in the visible region. However, this measurement was valid only for the films of intermediate thickness from 10 to 2 μm at 25°C; the infrared measurements were also made only in this thickness range. When being examined between two crossed polarizers, the film looked uniformly dark in this thickness range. Therefore the molecular orientation in this range at 25°C may correspond to that observed by Faetti and Fronzoni[1] in the range of 70–10 μm (homeotropic). The difference of the homeotropic thickness range found by the present authors and by Faetti and Fronzoni[1] is perhaps due to the difference of the experimental temperature. In Fig. 2, absorbances A of the 1626-, 1573-, and 833-cm^{-1} bands are plotted against the thickness of the nematic film of MBBA. These bands are assigned to the C=N stretching, the phenyl-ring stretching, and the phenyl CH out-of-plane deformation modes, respectively. The same plotting is also made for the isotropic (liquid) MBBA in Fig. 2. Apparently non-linear relations are observed for the nematic MBBA, while linear relations for the isotropic MBBA following the Lambert's low. This suggests that the molecular orientation in the nematic film varies with the film thickness.

Kelker, Hatz, and Wirzing[3] have reported a simple method to determine the orientation function for a uniaxial orientation of MBBA molecules with respect to the axis normal to the film surface. This method is based on measurements of the absorption of unpolarized light by homeotropic and isotropic films, and the orientation function f is given by the equation

$$f=1-R, \tag{1}$$

where R is the ratio of the absorbance of the homeotropic film to that of the isotropic film.

The orientation function for the homeotropic film of MBBA (2–10 μm) was calculated using this equation. The results are plotted against the film thickness in Fig. 3. Here (a), (b), and (c) refer to the 1626-, 1573-, and 833-cm^{-1} bands, respectively. The transition moments of the 1626- and 1573-cm^{-1} bands are reported to lie in the plane of the molecules and form the angles 32.1 and 10.5°, respectively, with the long axes of the molecules.[2] The transition moment of the 833-cm^{-1} band is normal to the plane of the benzene ring. It is apparent from Fig. 3 that the f values for the 1626- and 1573-cm^{-1} bands decrease but those for the 833-cm^{-1} band increase with increasing thickness. It is concluded therefore that the long axes of the molecules reduce the degree of orientation with respect to the normal axis to the film surface with increasing thickness of the film having two free surfaces in the range of 2–10 μm.

This calculation was quite simple, however, small dispersion of the experimental values of absorbance resulted in large dispersion of the orientation function as seen in Fig. 3. Thus, more quantitative discussions of the molecular orientation may not be allowed at this stage.

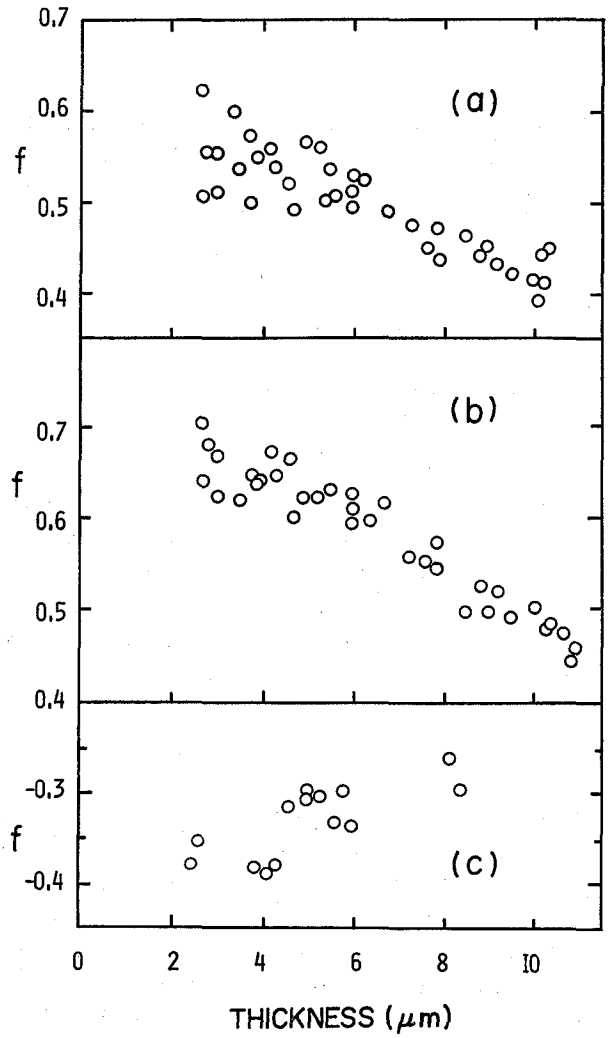

Fig. 3. Orientation function (f) *vs.* thickness plots for bands at (a) 1626, (b) 1573, and (c) 833 cm^{-1}.

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